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(54) Title: CONTROL OF HYDROGEN AND CARBON MONOXIDE PRODUCED IN PARTIAL OXIDATION PROCESS

(57) Abstract

A process for enhancing H_2 or CO production in a partial oxidation reaction by feeding H_2O or CO_2 with the feed hydrocarbon and oxygen over a transition metal monolith catalyst such as unsupported Ni monolith or alternatively contacting the hydrocarbon/oxygen first with a noble metal then with a transition metal with the H_2O or CO_2 being added before or after the noble metal catalyst. The addition of H_2O suppresses CO and enhances H_2 production and the addition of CO_2 suppresses H_2 and enhances CO production. Little steam or CO_2 reforming occurs with the addition of up to 32 % H_2O or CO_2 respectively. Thus, the ratio of H_2:CO which is about 2 in a conventional partial oxidation is manipulated by the addition of either water or CO_2 to the partial oxidation.

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CONTROL OF HYDROGEN AND CARBON MONOXIDE PRODUCED IN PARTIAL OXIDATION PROCESS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a process and apparatus for production of H_2 or CO by the partial oxidation of hydrocarbons, preferably methane. In particular the partial oxidation is carried out in the presence of water or carbon dioxide under water-gas shift reaction conditions. The invention was made with government support under DOE Grant No. DE-FG02-88ER13878-A02. The government has certain rights in the invention.

Related Art

Catalytic steam reforming of methane is currently the main industrial process to produce synthesis gas (CO and H_2). The steam reforming reaction may be represented as:

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

Reforming is highly endothermic, requiring energy input and also requiring contact times on the order of seconds. The resultant high H_2/CO ratio is also unsuitable for methanol and Fischer-Tropsch synthesis. Therefore additional downstream reactors are usually required to adjust this ratio by water-gas shift reaction at contact time of ≈1 second as:

$$CO + H_2O \longleftrightarrow H_2 + CO_2$$

Partial oxidation, on the other hand, is an exothermic reaction which can be represented by the reaction of methane with oxygen as follows:

$$CH_4 + \tfrac{1}{2}O_2 \longrightarrow CO + 2H_2$$

To produce synthesis gas by steam reforming, high temperature heat input is primarily required at two process steps. First, sufficient steam at a high temperature and high pressure must be generated for mixing with the hydrocarbon feedstock and, second, the steam reforming of the steam and hydrocarbon mixture must take place at relatively high temperatures and pressures through a bed of solid catalyst. The equipment needed for these two heat transfers at high temperature and high pressure is

necessarily quite expensive. The equipment for the steam reforming step is also costly because it must be adapted to permit the changing of the solid catalyst when that catalyst is spent or poisoned. Heat sources appropriate for the above two process steps are typically provided by fired heaters at high, continuing utility costs, also with high fluegas NO_x production consequential to the high temperatures required in the furnace firebox.

The production of synthesis gas by partial oxidation is considered a desirable alternative to steam reforming since it overcomes some of the problems of steam reforming, see for example PCT publication WO 90/06282 and WO 90/06297. U.S. Pat. No. 4,844,837 to Heck et al discloses a catalytic partial oxidation method for methane using a monolith catalyst with platinum-palladium, palladium-rhodium, or platinum-rhodium coatings. U.S. Pat. No. 4,087,259 to Fujitani et al describes a monolith catalyst with a rhodium coating to perform catalytic partial oxidation on gasoline and heavier petroleum fractions. U.S. Pat. No. 5,648,582 to Schmidt et al discloses the partial oxidation of methane at short residence times using metal deposited on a ceramic monolith.

In these conventional partial oxidations, methane (natural gas) is converted to high purity H_2 and CO with a mole ratio of H_2:CO $\approx$2.0, which is the desired feed ratio for methanol and Fischer-Tropsch plants. However, many other applications require different ratios of H_2:CO. The present synthesis gas shift reactor modifies the prior processes to obtain either high purity H_2 or CO.

Recent advancements in fuel cell technology have spurred an interest in converting natural gas into hydrogen. Pure hydrogen streams can be produced by steam reforming followed by high temperature shift using an Fe based catalyst, and low temperature shift using a Cu based catalyst. For natural gas to be an effective H_2 source for fuel cells, the present natural gas conversion technology must be simplified, preferably to a single, highly selective small catalytic reactor. Other applications

include acetic acid production, which requires pure CO feeds. We have discovered that the H_2:CO product ratio can be altered by the addition of CO_2 or H_2O through the water-gas shift reaction while the conversion of CH_4 remains constant, indicating negligible reforming is occurring.

SUMMARY OF THE INVENTION

Briefly, the present invention is a process for the partial oxidation of hydrocarbons such as methane (natural gas) by contacting a feed containing the hydrocarbon and oxygen and H_2O or CO_2 through a catalyst zone containing a catalytically effective amount of at least one transition metal monolith catalyst under partial oxidation conditions. A preferred monolith catalyst is a nickel metal monolith. When H_2O is fed, the product shifts toward the H_2 and when CO_2 is present the product shifts toward CO, thus the presence of either water or CO_2 provides the means to adjust the H_2:CO ratio, preferably in the range of more than about 2 to about 6 when water is added and in the range of less than about 2 to about 0.5 when CO_2 is added. It appears that the presence of water or CO_2 in the reaction zone according to the present invention produces a water-gas shift rather than reforming.

In a further embodiment the process comprises a first contacting a feed comprising methane and oxygen feed with or without H_2O or CO_2 with a noble metal coated onto a monolith. The H_2O or CO_2 may be fed through the noble metal monolith or between the noble metal monolith and the transition metal monolith.

Because partial oxidation reactions are exothermic, it is not necessary to add external heat to the system other than to obtain ignition of the catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the conversion of CH_4 and selectivities to H_2 with CO_2 addition over Ni.

Fig. 2 shows the conversion of CH_4 and selectivities to H_2 with CO_2 addition over Rh.

Fig. 3 shows the conversion of CH_4 and selectivities to H_2 with CO_2 addition over Pt.

Fig. 4 shows the conversion of CH_4 and selectivities to CO with H_2O addition over Ni.

Fig. 5 shows the conversion of CH_4 and selectivities to CO with H_2O addition over Rh.

Fig. 6 shows the conversion of CH_4 and selectivities to CO with H_2O addition over Pt.

Fig. 7 compares the selectivity to CO in the product with the addition of H_2O over Ni, Rh, and Pt.

Fig. 8 compares the ratio of the H_2 in the product to the CH_4 in the feed with the addition of H_2O over Ni, Rh, and Pt.

Fig. 9 compares the ratio of CO/CO_2 in the product with the addition of H_2O over Ni, Rh and Pt.

Fig. 10 compares the conversion of CH_4 with the addition of H_2O over Ni, Rh, and Pt.

Fig. 11 discloses a single bed catalyst reaction system according to the present invention.

Fig. 12 discloses a multibed catalyst reaction system according to the present invention.

Fig. 13 discloses an alternative multibed catalyst reaction system according to the present invention.

DETAILED DESCRIPTION

The present catalyst is comprised of a monolith structure either composed of the metal of the catalyst or coated with the metal of the catalyst. The metals may be in the oxide form during use in the present process. The thickness of the monolith through which the feed gas mixture must pass is from 1 mm to 2 cm. Catalyst contact time ranges from 0.1 to 20 milliseconds when using a monolith of 50% porosity and 0.2 to 1 cm in depth. Under operating conditions, this corresponds to Gas Hourly Space Velocity (GHSV) of 60,000 to 3,000,000 hr^{-1}.

Ceramic foam monoliths have been found in the present invention to create the superior mass transfer characteristics necessary if high space velocities are to be used. The metal monolith may be prepared as metal foam or sintered particles of metal. The solid metal monoliths exhibit superior heat transfer properties but may require

substantial amounts of very expensive metals in some embodiments. Thus, in some applications the metal coated ceramics will be the catalyst of choice. As used herein the term "metal monolith" shall include both the solid metal monoliths and the metal coated ceramic monoliths. The solid metal monoliths may be produced by any method, for example foaming, sintering and fusing.

The reactor is started from ambient temperature through the use of a mixture of light hydrocarbons or ammonia and air preheated to about 200°C and then introduced to the monolith catalyst at an appropriate temperature at which combustion will occur. After combustion has established a monolith catalyst temperature of near 1000°C, preheat and ammonia is stopped. The feed gas mixture of hydrocarbons (methane) and oxygen is then fed to the catalyst zone at a temperature of from 25° to 450°C. Thus, the gas feed mixture of the present invention does not require preheating to near its ignition temperature prior to introduction to the catalyst, thereby avoiding the production of CO_2 and H_2O and the concurrent reduction of the selectivity for H_2 and CO. With the introduction of water or carbon dioxide to the reaction in accordance with the present invention, the preheat of the feed is adjusted to maintain the established outlet temperature.

The amounts of hydrocarbon, H_2O, CO_2 and oxygen introduced into the partial oxidation (catalyst zone) are controlled to provide O_2:C ratios of from about 0.2 to 0.8 and H_2O or CO_2:C ratios of about 0.5 to 5. The process is carried out from about atmospheric pressure to about 2000 psig. The amount of water or CO_2 added is preferably up to 45%, more preferably 5 to 35% of the gaseous feed.

Because the hydrocarbon conversion remains constant with or without the H_2O or CO_2 it appears that little or no reforming is occurring. Thus the present partial oxidation in the presence of H_2O or CO_2 is characterized as occurring in the substantial absence of reforming. The predominant reaction in the presence of water or CO_2 is characterized as a water-gas shift reaction.

In a preferred embodiment of the present invention, catalytic partial oxidation, an exothermic reaction, takes place in a catalyst monolith having a specified transition metal alone or preceded by a noble metal dispersed to produce a gas which is rich in carbon monoxide and hydrogen. The reaction in the catalytic partial oxidation zone is exothermic and the zone is therefore also referred to as an exothermic catalyst zone. The exothermic, catalytic partial oxidation zone comprises either solid metal monolith and/or a monolithic catalyst carrier or carriers on which transition or transition and noble metal catalyst is dispersed. Such catalyst can effectively catalyze the partial oxidation of, in addition to, gaseous and lighter hydrocarbon liquids such as natural gas or paraffinic naphtha, heavier hydrocarbon liquids such as diesel oil, number 2 fuel oil, and coal derived liquids. As compared to a non-catalytic combustion process such as conventional, non-catalytic partial oxidation, catalytic partial oxidation as described above enables the utilization of lesser amounts of oxygen and lower temperature levels to both oxidize a portion of the feed and crack heavier feedstocks to lighter hydrocarbon fractions while raising the temperature of the reactant mass for subsequent treatment. Generally, at least about half the hydrocarbon feed stock is partially oxidized in the catalytic partial oxidation zone to produce primarily carbon monoxide and hydrogen and heat. Substantially all of the oxygen introduced into the catalytic partial oxidation zone is consumed in the partial oxidation step. The oxygen introduced into the catalytic partial oxidation zone is consumed in the catalytic partial oxidation step. The oxygen may be provided by any suitable "oxygen-containing oxidant gas" which term is used in the claims to include air, air enriched with oxygen, oxygen or oxygen mixed with other gases. The effluent gas from the catalytic partial oxidation zone contains primarily CO, H_2, H_2O, N_2, C_2 to C_4 and other lighter hydrocarbons, including olefins, and, depending upon the sulfur content of the feedstock, H_2S and

COS. Methane is the preferred feed for H_2 or CO production.

The presence of H_2O (steam) results in a favorable shift in the product of the H_2:CO ratio to H_2, whereas the presence of CO_2 shifts the ratio in favor of CO.

The combination of features provided by the present invention provides a highly efficient and flexible method of converting various types of hydrocarbonaceous feeds to a hydrogen-rich gas. For example, the combination of features provided by the process of the present invention provides a highly efficient process of manufacturing a synthesis gas by converting various types of hydrocarbonaceous feeds, including hydrocarbon feeds, to a nitrogen and hydrogen-rich gas suitable for use in ammonia synthesis. By utilizing the catalytic partial oxidation process as described, a wide variety of hydrocarbonaceous feeds may be efficiently and economically converted into a hydrogen-rich gas.

The Monolithic Partial Oxidation Catalysts

The partial oxidation catalyst either comprises or is supported on a monolithic carrier, that is, a carrier of the type comprising one or more monolithic bodies having a plurality of finely divided gas flow passages extending therethrough. Such monolithic carrier members are often referred to as "honeycomb" type carriers and are well known in the art. A preferred form of such carrier is made of a refractory, substantially inert, rigid material which is capable of maintaining its shape and a sufficient degree of mechanical strength at high temperatures, for example, up to about 3,373°F. (1,856°C.). Typically, a material is selected for the support which exhibits a low thermal coefficient of expansion, good thermal shock resistance and, though not always, low thermal conductivity. Two general types of material for construction of such carriers are known. One is a ceramic-like porous material comprised of one or more metal oxides, for example, alumina, alumina-silica, alumina-silica-titania, mullite, cordierite, zirconia, zirconia-spinal, zirconia-mullite,

silicon carbide, etc. A particularly preferred and commercially available material of construction for operations below about 2,000°F. (1,093°C.) is cordierite, which is an alumina-magnesia-silica material. For applications involving operations above 2,000°F. (1,093°C) an alumina-silica-titania material is preferred. Honeycomb monolithic supports are commercially available in various sizes and configurations. Typically, the monolithic carrier would comprise, e.g., a cordierite member of generally cylindrical configuration (either round or oval in cross section) and having a plurality of parallel gas flow passages or regular polygonal cross section extending therethrough. The gas flow passages are typically sized to provide from about 50 to 1,200, preferably 200 to 600, gas flow channels per square inch of face area.

Various honeycombed (reticulated) ceramic structures are described in the art: U.S. Pat. No. 4,251,239 discloses fluted filter of porous ceramic having increased surface area; U.S. Pat. No. 4,568,595 discloses honeycombed ceramic foams with a surface having a ceramic sintered coating closing off the cells; U.S. Pat. No. 3,900,646 discloses ceramic foam with a nickel coating followed by platinum deposited in a vapor process; U.S. Pat. No. 3,957,685 discloses nickel or palladium coated on a negative image ceramic metal/ceramic or metal foam; U.S. Pat. No. 3,998,758 discloses ceramic foam with nickel, cobalt or copper deposited in two layers with the second layer reinforced with aluminum, magnesium or zinc; U.S. Pat. No. 4,863,712 discloses a negative image honeycombed (reticulated) foam coated with cobalt, nickel or molybdenum coating; U.S. Pat. No. 4,308,233 discloses a reticulated ceramic foam having an activated alumina coating and a noble metal coating useful as an exhaust gas catalyst; U.S. Pat. No. 4,253,302 discloses a foamed ceramic containing platinum/rhodium catalyst for exhaust gas catalyst; and U.S. Pat. No. 4,088,607 discloses a ceramic foam having an active aluminum oxide layer coated by a noble metal containing composition such as zinc oxide, platinum and

palladium.

The foam structure is characterized by the number of pores per linear inch and typical foams are produced with 10 to 100 pores per linear inch. The ceramic supports employed in the present invention are generally of the type disclosed in U.S. Pat. No. 4,810,685 using the appropriate material for the matrix and are generally referred to in the art and herein as "monoliths".

Generally any organic liquid in which the metal salt is soluble may be used to deposit metals on to monolith supports. The metals may also be deposited from aqueous solutions using the water soluble salts.

Generally from 0.5 to 20 wt % of the metal will be deposited on the monolith (based on the weight of monolith).

A suitable high surface area refractory metal oxide support layer may be deposited on the carrier to serve as a support upon which finely dispersed catalytic metal may be distended. As is known in the art, generally, oxides of one or more of the metals of Groups II, III, and IV of the Periodic Table of Elements having atomic numbers not greater than 40 are satisfactory as the support layer. Preferred high surface area support coatings are alumina, beryllia, zirconia, baria-alumina, magnesia, silica, and combinations of two or more of the foregoing.

The most preferred support coating is alumina, most preferably a stabilized, high-surface area transition alumina. One or more stabilizers such as rare earth metal oxides and/or alkaline earth metal oxides may be included in the transition alumina (usually in amounts comprising from 20 to 10 weight percent.

The metal monolith may be prepared as metal foam or sintered particles of metal at high temperature. Monolithic supports may also be made from materials such as nickel or stainless steel by placing a flat and a corrugated metal sheet, one over the other, and rolling the stacked sheets into a tubular configuration about an axis parallel to the corrugations, to provide a cylindrical-

shaped body having a plurality of fine, parallel gas flow passages extending therethrough.

The transition metals useful in the present invention are selected from the groups consisting of Fe, Os, Co, Rh, Ir, Ni Cu, Pd, Pt and mixtures thereof, with Fe, Co, Ni or Cu forming a preferred grouping, more preferably Ni and more preferably as a solid nickel monolith. Nickel supported on alumina monoliths was not found to be useful in the present process.

The noble metals useful in the present invention are selected from the group consisting of Ru, Rh, Pd, Pt and mixtures thereof preferably Pt or Pd.

For Figs. 1-10 runs were carried out in a quartz tube continuous reactor with 18 mm diameter. Identical α-Al_2O_3 monoliths without metal were positioned before and after the catalyst to reduce radiation losses. The catalyst and radiation shields were sealed in the quartz reactor by silica-alumina cloth. The temperatures of the front and back sides of the catalyst were measured with Pt-Pt/Rh thermocouples placed between the catalyst and the radiation shields. Rh and Pt catalysts were ignited with a Bunsen burner at a CH_4/O_2 ratio of 1.8. The fresh Ni spheres were more difficult to ignite, and therefore NH_3 was added to the feed to lower ignition temperature. After ignition, the reactor was insulated by wrapping it in high temperature insulation.

Rh and Pt catalysts were prepared by impregnating α-Al_2O_3 foam monoliths (18 mm diameter by 10 mm long) with concentrated metal salt solutions (rhodium chloride in acetone or chloroplatinic acid in H_2O) which were added dropwise to the monolith and allowed to dry overnight. The samples were further dried at 390 K for 2 hours and then calcined at 870° K for 2 hours in He and reduced at the same temperature in 10% H_2/Ar for 7 hrs. However, spheres of sintered Ni activated over a period of 6 hours (at normal reaction conditions) catalyzed an oxidation reaction in which the conversion and selectivities steadily increased. Therefore pure sintered Ni metal spheres (Alfa,

-40 mesh, deposition grade, 99.9%) packed to 1 cm deep were used directly. Similar results were obtained with foamed nickel monolith.

Flow rates of high purity O_2, N_2, CO_2 and CH_4 were controlled by mass flow controllers with an accuracy of $\pm$0.01 standard liters per minute (slpm). Initial experiments with no CO_2 or H_2O added to the feed were conducted at 4 slpm, CH_4/O_2= 1.8 and 35% dilution, which is optimal fuel/oxygen ratio for syngas production. For all of the CO_2 results presented here, the N_2 was replaced by CO_2 to maintain a constant contact time within the catalyst. The exit temperature of the catalyst was held constant by preheating the feed gases. Runs were repeated where CO_2 was added to a constant flow of CH_4, O_2 and N_2. These results are nearly identical and show the same trends as the data presented here and are omitted. For runs in which steam was added to the feed, water was supplied by a syringe pump through a two stage vaporizer and a back pressure regulator to eliminate system pulsing. In all results reported, H_2O was added to a constant flow of CH_4, O_2 and N_2.

Product gases were analyzed by a HP 5890 gas chromatograph with a thermal conductivity detector and integrated by an on-line computer. The detected reaction products were H_2, CO, CO_2 and H_2O on all catalysts, and over Pt up to 1% C_2 products were observed. CH_4 conversion and products selectivities were calculated as described previously. For CO_2 addition, the selectivities to CO and CO_2 are not reported (the only carbon containing product that is not a reactant is CO). Similarly H_2 and H_2O selectivities are not reported for H_2O addition. In all runs the carbon and hydrogen balances closed with an accuracy better than 97%.

Figs. 1-3 show the conversions of CH_4 and selectivities to H_2 with CO_2 addition on Ni, Rh and Pt catalysts. The reaction temperatures on Ni, Rh and Pt catalysts were held constant with CO_2 addition, 1240°, 1250° and 1500° K, respectively. The equilibrium predictions of CH_4

conversion and H_2 selectivities at these temperatures are shown by the dashed lines. Since Pt produces a lower H_2/H_2O ratio, its temperature is ≈250°C hotter than Ni or Rh.

The CH_4 conversions were nearly constant up to 30% CO_2 addition on all three catalysts, but significantly lower than the equilibrium CH_4 conversions which is nearly 100%. These results imply that little CO_2 reforming of CH_4 occurs at contact times of ≈5 ms and ≈1300°K. Fig 1 also shows that the conversion of CH_4 is higher on Rh (80%) than on Ni (72%) with Pt (54%) being much less active.

The addition of CO_2 decreases the selectivity to H_2 over all three catalysts, but to very different amounts. With 24% CO_2 addition on Ni, the H_2 selectivity decreases from 80% to 55%, on Rh it decreases from 84% to 67%, and on Pt it decreases from 59% to 41%. The H_2 selectivities are roughly parallel to, but lower than, the calculated equilibrium H_2 selectivities. These results indicate that CO_2 reacts with H_2 in the reverse water-gas shift reaction to a greater extent on Ni and least on Pt.

Addition of H_2O

The results of H_2O addition with a constant flow of CH_4, O_2, and N_2 over Ni, Rh or Pt are shown in Figs. 4-6. In these runs, the temperature was kept constant at the adiabatic temperature in the absence of H_2O by preheating the gas stream. Because of preheat limitations, maintaining a constant temperature on the Pt catalyst at greater than 12 Vol% H_2O feed was difficult and therefore is not reported.

Figs. 4-6 show that the CH_4 conversions were nearly constant over the entire range of H_2O addition on all three catalysts, indicating that negligible steam reforming of CH_4 is occurring under these conditions.

As H_2O is added to the feed the selectivity to CO decreases on Ni and Rh but remains essentially constant over Pt. On Ni, the selectivity to CO decreases from 88% to 50% while on Rh the selectivity only drops from 94% to 87%. The H_2O seems to be reacting with CO by the water-gas

shift reaction over Ni and Rh but not over Pt.

The present results exhibited no catalyst deactivation on unsupported Ni and on supported Pt and Rh for over 100 hours of operation at atmospheric pressure. The present data also show that as the concentration of CO_2 in the feed increases, the conversion of CH_4 remains constant. This clearly shows that CO_2 reforming is not occurring significantly at temperatures near 1300° K, at contact times near 1 ms and in the presence of oxygen.

Although these results may seem contradictory to previous literature, three distinct factors differentiate this work from previous results. First, the present reactor runs adiabatically and autothermally, therefore the reaction temperature is controlled by the catalyst selectivity and the temperatures typically run 250 to 500° hotter than typical CO_2 reforming runs. Second, the contact time over the catalyst in our runs is approximately 1 ms, corresponding to a gas hourly space velocity GHSV of $\sim 1\times10^5 h^{-1}$, which is approximately a factor of 10 higher than most previous CO_2 reforming work. Finally, the presence of O_2 may inhibit CO_2 reforming reactions. The CH_4 is probably reacting with O_2 very rapidly, and the extremely short contact times prevent the remaining CH_4 from reacting with CO_2.

Similar results have been reported by Choudhary et al, Catal. Lett. 32 (1995) 391-396 over NiO-CaO catalyst at space velocities of up to $5\times10^5 cm^3\ g^{-1}\ h^{-1}$ and temperatures up to 900°C. For CO_2 reforming in the absence of O_2, the NiO-CaO catalyst coked very rapidly, but when O_2 is added to the feed, the catalyst showed no deactivation due to coke formation. They used their results to show that the addition of O_2 overcomes the endothermic limitations of CO_2 reforming by initially combusting part of the CH_4. The energy released by combustion can then be immediately used to drive the reforming reactions. They confirmed this by calculating the ratio of CO_2 reforming to oxidative conversion of CH_4 based on the chemistry being controlled by three reactions: 1) partial oxidation of CH_4 with O_2 to

syngas, 2) complete combustion of CH_4, 3) and CO_2 reforming of CH_4.

Although, this may be a valid explanation of the product distribution in these experiments, it is believed that present results are better described by the direct oxidation of CH_4 to syngas followed by water-gas shift. Figs. 1-3 show that as CO_2 is added to the feed, the conversion of CH_4 does not change when the outlet temperature is held constant, for example by preheating the feed, indicating that CO_2 reforming of CH_4 is probably not active at these contact times and temperatures. However, as CO_2 is added the selectivity to H_2 decreases over all three metals. This implies that CO_2 is reacting with H_2 in the reverse water-gas shift.

The present results show that the water-gas shift reaction is being affected by the addition of H_2O, particularly over the Ni monolith. H_2O seems to be reacting with CO in the forward water-gas shift to form CO_2 and H_2. The combination of the CO_2 and H_2O addition results strongly confirm the activity of the water-gas shift reaction and its reverse at >1000° K and 1 ms contact time.

As with CO_2 reforming, steam reforming seems to be inactive over Ni, Rh or Pt at high temperatures and millisecond contact times. This is probably because the CH_4 preferentially reacts with O_2 first, and the remaining CH_4 does not react with the H_2O at these extremely short contact times. This is expected from the relatively low sticking coefficients of CO_2 and H_2O compared to O_2.

The present results show that addition of CO_2 or H_2O to the feed stream affects the selectivity to H_2 and CO but leaves the conversion of CH_4 unaffected. The short contact times, 10 to 10 ms, do not allow significant CO_2 or steam reforming on any of the three metals, and the dominant reaction is the direct oxidation of CH_4 to CO and H_2.

Since the H_2 selectivity decreases with the addition of CO_2 (or CO selectivity decreases with the addition of H_2O), the water-gas shift reaction or its reverse must be active

at present reaction temperatures and contact times. Therefore, it is believed that the direct partial oxidation of CH_4 to syngas followed by the water-gas shift reaction are the dominant reactions in the present invention.

Figs. 1-6 show that at contact times near 1 ms, the direct partial oxidation of methane to syngas appears to be followed by water-gas shift or its reverse. Because the water-gas shift reaction is active at 1300° K and 1 ms, the product selectivities can be tuned from high CO to high H_2 content by introducing CO_2 or H_2O respectively into the feed stream.

The negligible steam or CO_2 reforming occurs in the presence of O_2 over unsupported Ni and α-Al_2O_3 supported Rh and Pt catalysts at contact times of 1-10 ms and 1300 K. However, the water-gas shift reaction and the reverse shift reaction are active over Ni and Rh, with Pt being less active. Over Ni, the CO/CO_2 ratio decreases to 1 at 30% H_2O addition, which tranlates to a H_2/CO ratio of 5. This demonstrates the addition of H_2O or CO_2 can be used to manipulate the ratio of H_2/CO in the product stream.

In Fig. 11 an apparatus with a single transition metal catalyst is illustrated. Hydrocarbon/O_2 flow 8 is in the direction of the arrow into tubular reactor 10. H_2O (as steam) or CO_2 enters via line 12 into a bead packing 22. The tubular reactor 10 is wrapped with heating tape and the catalyst 14 is sandwiched between two heat shields 16 and insulated by 18.

In Fig. 12 an apparatus with a multi-catalyst zone is shown in tubular reactor 100. Hydrocarbon/O_2 feed enters 108 in the direction of the arrow to flow through the reactor. H_2O (steam) or CO_2 enter into beads 122 via 112 and the mixture contacts noble metal catalyst 114 then transition metal (preferred group) 115. The two catalyst monoliths are associated with heat shields 116 and insulated by 118. The front portion of the reactor containing the beads is wrapped with heating tape 120.

Fig. 13 is a modification of the apparatus of Fig. 12.

The hydrocarbon/O_2 feed 208 enters the tubular reactor 200 and passes through noble metal monolith catalyst 214 which is sandwiched between heat shields 216. That section is insulated by 218. The reaction has been initiated by igniting the catalyst 214. The product from this partial oxidation passes into the bead packing 222 where it mixes with H_2O (steam) or CO_2 entering via 212. The mixture proceeds through transition metal (preferred group) monolith catalyst 215. Heating tape is provided to maintain the temperature from the exothermic partial oxidation.

It has been found that unsupported metal monoliths such as nickel monolith is advantageous over ceramic supported metals. Because of the high thermal conductivity of Ni, the monolith is a better thermostat and higher flow rates can be achieved with similar selectivities and conversions. By using unsupported Ni, the possibility of nickel-aluminate formation and therefore a deactivation route is eliminated. These two advantages combined allow for operation over wider range of inlet conditions.

The multiple catalyst bed design takes advantage of a more selective catalyst for synthesis gas formation. In this design the first bed is a supported noble metal catalyst, preferably Rh. This catalyst is supported by a reticulated or extruded ceramic structure and the weight loadings of catalyst can range from 0.1% to in excess of 10%. Steam or CO_2 is injected immediately following the first catalyst bed prior to entering the second bed. The second bed requires energy input to maintain reaction. This catalyst can be a noble metal, transition metal or metal oxide, like Ni, Fe, or Cu.

To initiate reaction, the feed gases are introduced to the reactor at the desired flow rate and composition. Energy is added to the catalyst either electrically or thermally until the catalyst ignites. After catalyst ignition the energy source is removed, and preheat is the only external energy source required to maintain reaction temperatures between 800° and 1000°C. For the multi-bed

reactor, the second and beyond stages may need to be maintained at temperature either by external heating or from the energy released in the first stage.

Gas hourly space velocities $\sim 10^5 h^{-1}$ have been used for the process. Inlet compositions of fuel and oxygen were taken from literature sources for the optimal production of synthesis gas. Natural gas was simulated by CH_4, the dominant component of natural gas. The inlet compositions ranged from 64% fuel, 36% oxidant to 35% fuel, 20% oxidant and 45% H_2O or CO_2.

The introduction of H_2O into the feed stream results in a decrease in the CO/CO_2 ratio. With no H_2O the $CO:CO_2$ ratio is 8:1, but with 40% H_2O feed the ratio is reduced to 1.3:1 when using an unsupported bed of nickel. Adding CO_2 instead of H_2O results in a decrease in the $H_2:H_2O$ ratio from 9:1 to 1:1 again over a nickel catalyst. Similar results have been demonstrated over Rh and Pt catalysts.

The invention claimed is:

1. A process for the partial oxidation of hydrocarbons by feeding a stream containing hydrocarbon, oxygen and H_2O or CO_2 through a catalyst zone containing a catalytically effective amount of at least one transition metal monolith catalyst under partial oxidation conditions wherein said transition metal is selected from the group consisting of Fe, Ru, Os, Co, Rh, Ir, Ni, Cu, Pd, and Pt.

2. The process according to claim 1 wherein the transition metal is Ni or Rh.

3. The process according to claim 1 wherein said catalyst comprises a nickel metal monolith.

4. The process according to claim 1 wherein said catalyst zone contains one transition metal catalyst.

5. The process according to claim 4 wherein the transition metal is Ni or Rh.

6. The process according to claim 1 wherein H_2O is fed with said hydrocarbon and oxygen.

7. The process according to claim 1 wherein CO_2 is fed with said hydrocarbon and oxygen.

8. The process according to claim 1 wherein at least said hydrocarbon and said oxygen are contacted with a noble metal monolith catalyst under partial oxidation conditions prior to contacting said transition metal monolith catalyst wherein said noble metal is selected from the group consisting of Ru, Rh, Pd, Ir, and Pt.

9. The process according to claim 8 wherein H_2O is fed with said hydrocarbon and oxygen to contact said noble metal catalyst.

10. The process according to claim 8 wherein CO_2 is fed with said hydrocarbon and oxygen to contact said noble metal catalyst.

11. The process according to claim 8 wherein said H_2O is fed to said stream after said noble metal monolith catalyst and prior to said transition metal monolith catalyst.

12. The process according to claim 8 wherein said CO_2 is fed to said stream after said noble metal monolith

catalyst and prior to said transition metal monolith catalyst.

13. The process according to claim 1, 4, 6, 7, 8, 9, 10, 11, or 12, wherein said transition metal is selected from the group consisting of Fe, Ru, Os, Co, Rh, Ir, Ni, and Cu.

14. The process according to claim 13 wherein said transition metal is Fe, Cu, or Ni.

15. The process according to claim 14 wherein said transition metal is Cu.

16. The process according to claim 14 wherein said transition metal is Ni.

17. The process according to claim 8, 9, 10, 11, or 12, wherein said noble metal is selected from the group consisting of Pd and Pt.

18. The process according to claim 17 wherein said noble metal is Pt.

19. The process according to claim 17 wherein said noble metal is Pd.

20. The process according to claim 3 wherein said nickel monolith comprises a foam.

21. The process according to claim 3 wherein said nickel monolith comprises sintered nickel particles.

22. The process according to claim 1 wherein the feed gas to the reaction is preheated to a temperature in the range of 25-450°C.

23. The process according to claim 22 wherein the pressure of the process is in the range of atmospheric to 2000 psig.

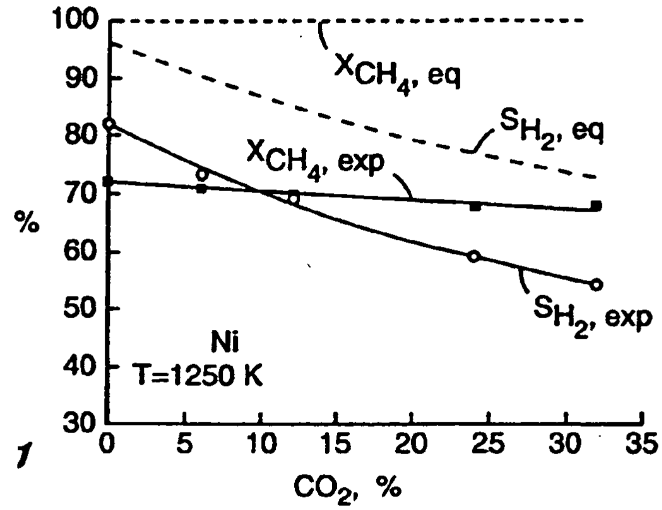

Fig. 1

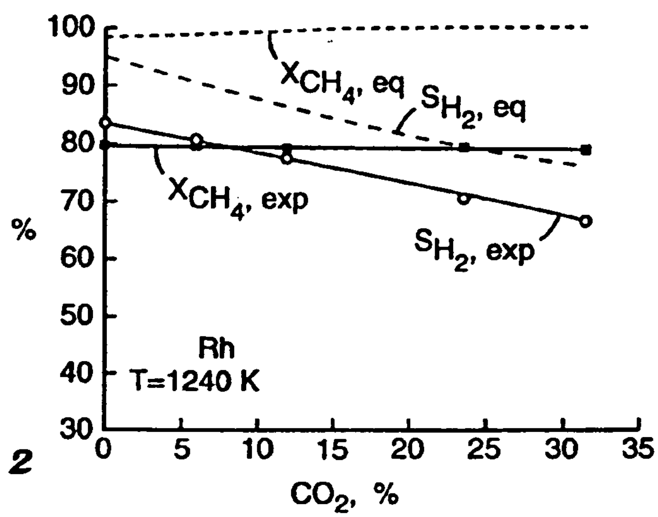

Fig. 2

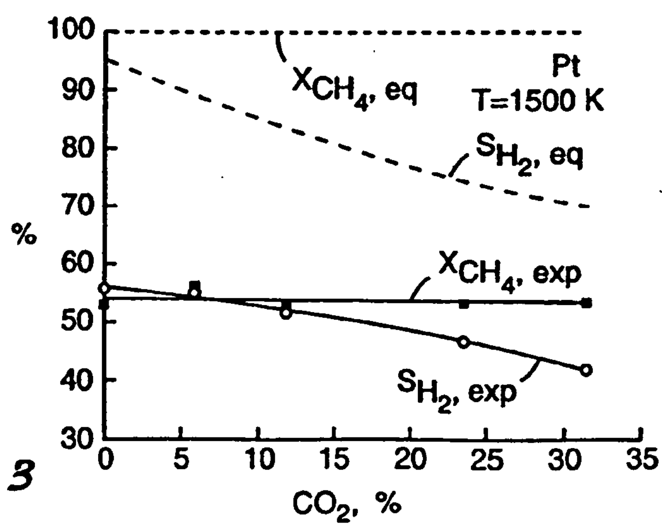

Fig. 3

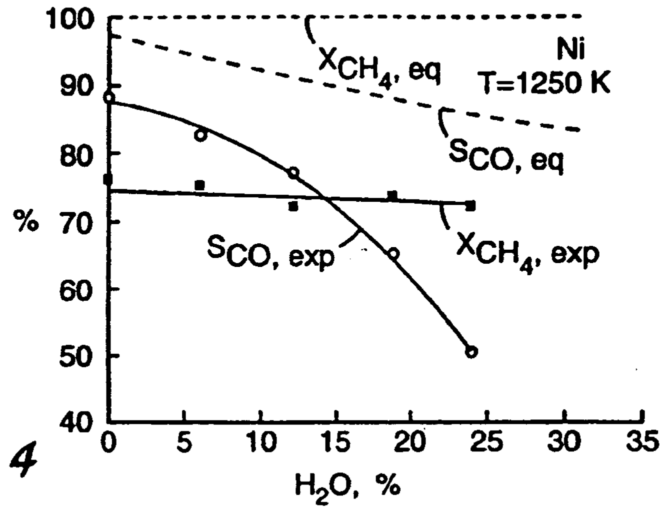

Fig. 4

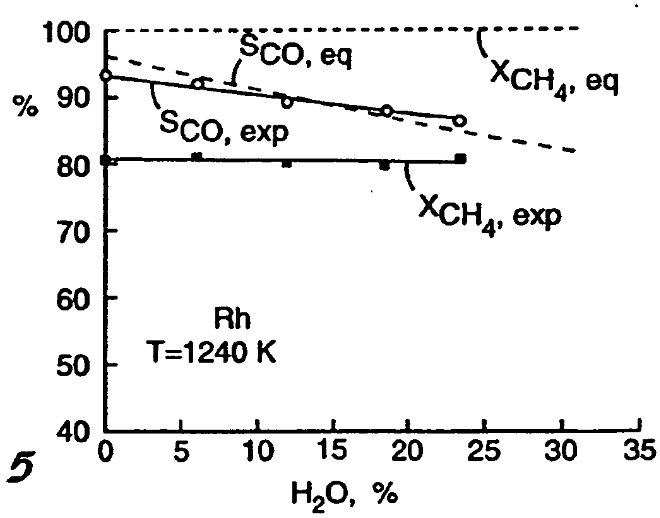

Fig. 5

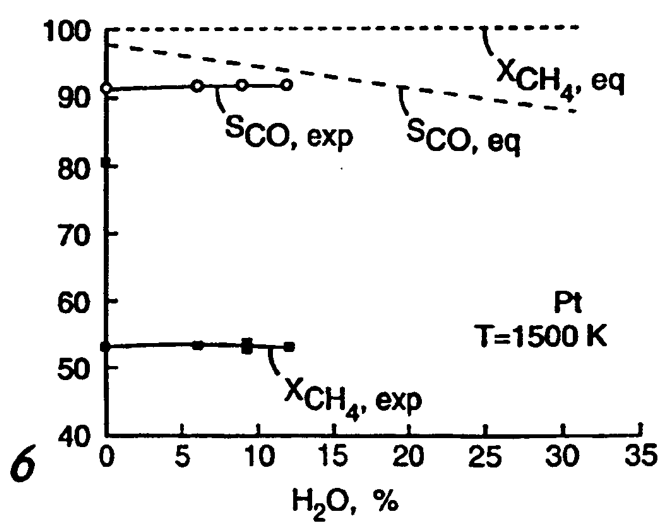

Fig. 6

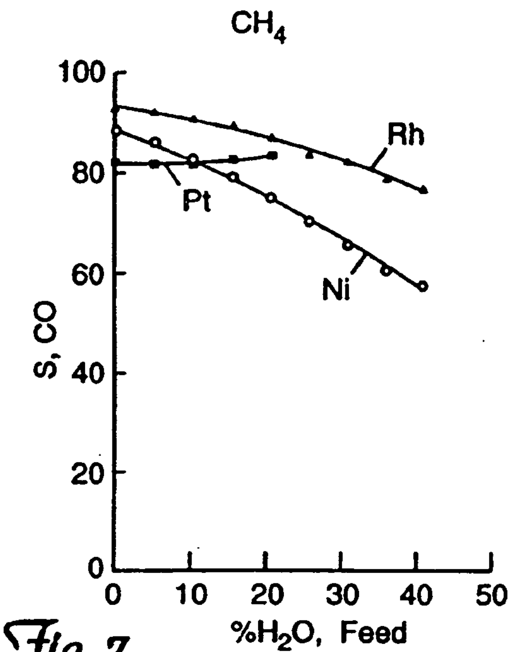

Fig. 7

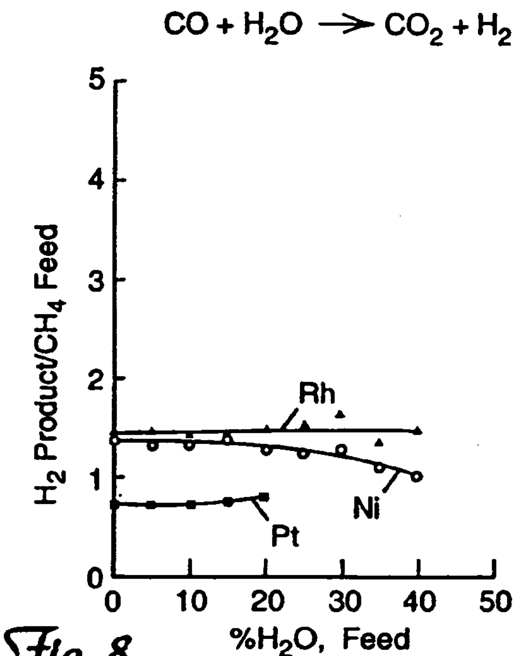

Fig. 8

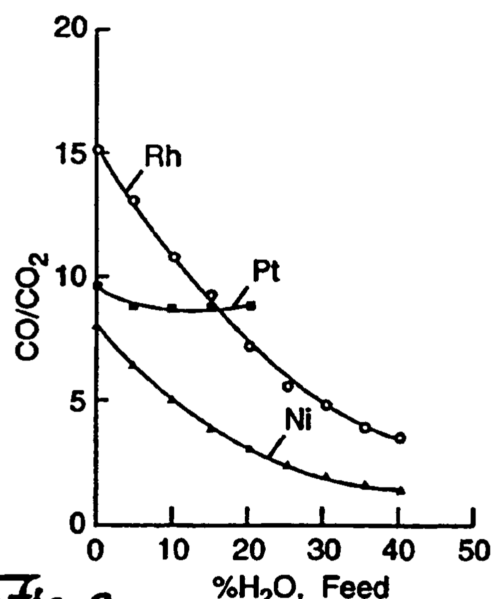

Fig. 9

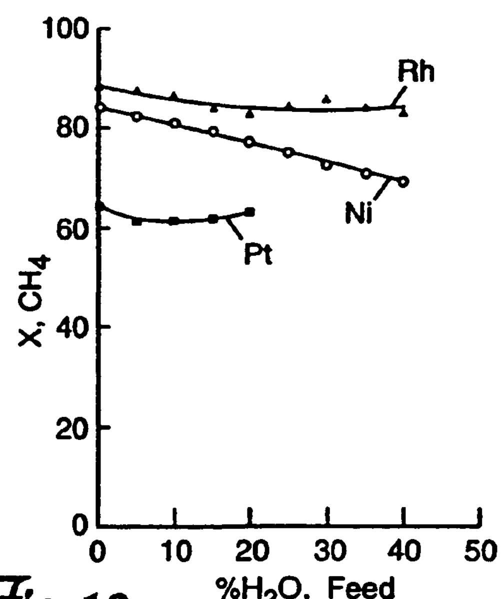

Fig. 10

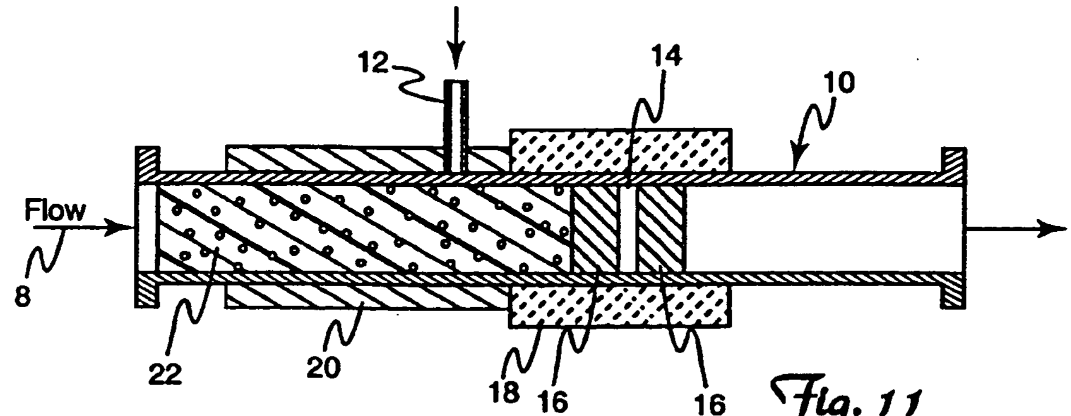

Fig. 11

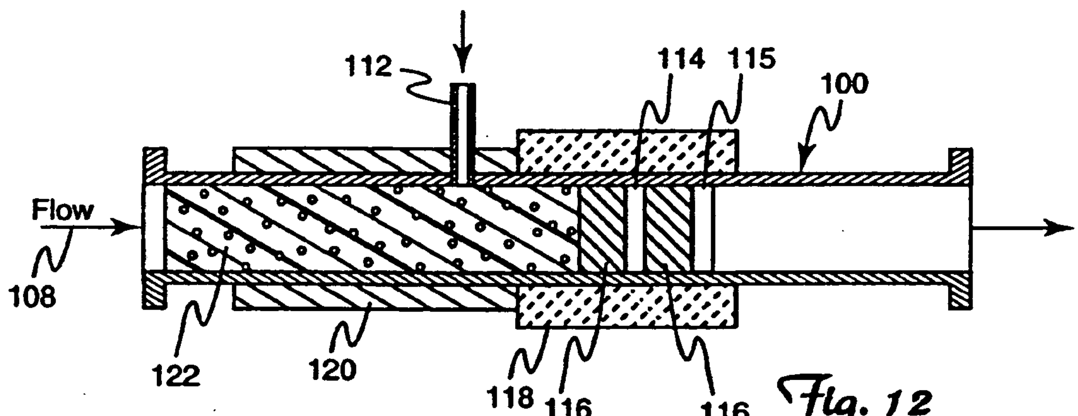

Fig. 12

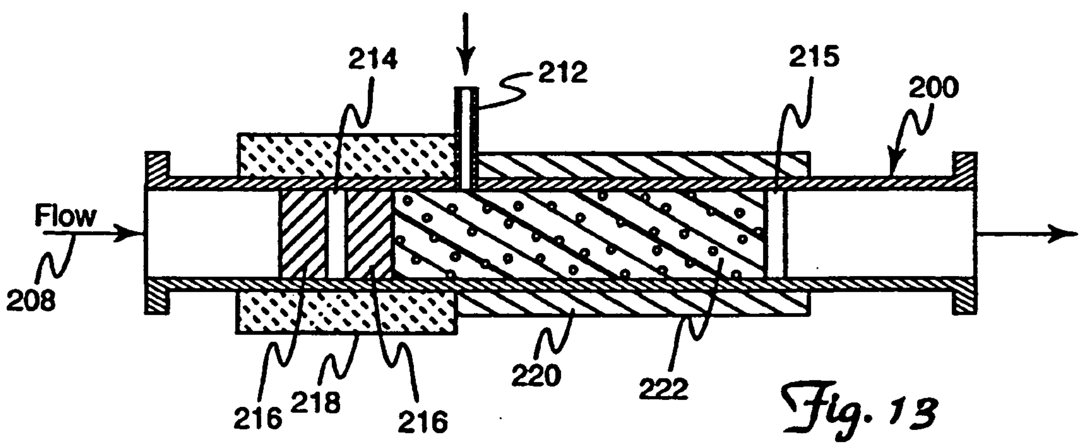

Fig. 13

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/00629

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B3/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 274 284 A (SNAM PROGETTI) 20 July 1994 see page 7, line 16 - page 11, line 10 ---	1-10,12, 13,16-23
X	EP 0 645 344 A (SHELL INT RESEARCH) 29 March 1995 see page 3, line 17 - page 4, line 58 ---	1-7,13, 14,16, 22,23
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 April 1999	27/04/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van der Poel, W

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INTERNATIONAL SEARCH REPORT

Int. ational Application No
PCT/US 99/00629

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	V. R. CHOUDHARY ET AL.: "Energy efficient methane-to-syngas conversion with low H2/CO ratio by simultaneous catalytic reactions of methane with carbon dioxide and oxygen" CATALYSIS LETTERS , vol. 32, 1995, pages 391-396, XP002099617 BASEL; SWITZERLAND cited in the application see the whole document ---	1-5,7, 13,14,16
X	WO 92 11199 A (ISIS INNOVATION) 9 July 1992 see examples -----	1-5,7, 13,14,16

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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

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